

# PATENT SPECIFICATION

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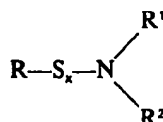


## (54) NOVEL SULPHENAMIDES

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

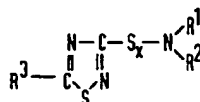
This invention relates to novel thio- and polythio sulphenamides of thiadiazoles.

The present invention therefore provides compounds of the general formula

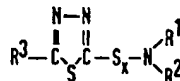


where X is from 2 to 5 and R is a 1,2,4 or 1,3,4-thiadiazole nucleus which may be substituted and R<sup>1</sup> and R<sup>2</sup> are hydrogen or hydrogen and carbon containing groups providing R<sup>1</sup> and R<sup>2</sup> are not both hydrogen or R<sup>1</sup> and R<sup>2</sup> form a heterocyclic ring with the nitrogen to which they are attached.

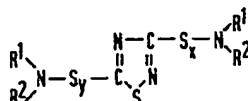
Thus the novel compounds of our invention may be of the formula



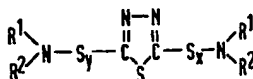
or of the formula



where R<sup>3</sup> may be hydrogen or a substituent including, hydrocarbyl groups or another sulphenamide or thiosulphenamide group. We have found these latter compounds to be particularly interesting and thus one preferred species of the present invention is compounds of the general formula



Another preferred species is compounds of the general formula



where X and R<sup>1</sup> and R<sup>2</sup> are as defined above and y is from 1 to 5.

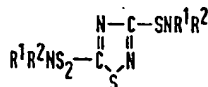
As mentioned above  $R^1$  and  $R^2$  may be same or different and may be hydrogen or hydrogen and carbon containing groups, providing both  $R^1$  and  $R^2$  are not hydrogen atoms. Particularly suitable sulphenamides are those where  $R^1$  and  $R^2$  are either both alkyl groups or where  $R^1$  is hydrogen and  $R^2$  is alkyl.

Where  $R^3$  is a sulphenamide or thiosulphenamide group the compounds of our invention can be mixtures of compounds having different values of X and Y. For example, where R is the 1,2,4-thiadiazole nucleus and X and Y are 1 or 2 our compound may be a mixture containing



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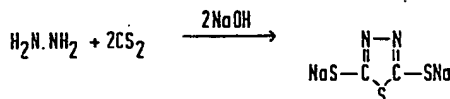
and



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and possibly higher homologues with varying sulphur content. The exact content will depend on the manufacturing process used. The similar mixtures based on the 1,3,4-thiadiazole nucleus may also be obtained.

The preferred thio-sulphanamides of the present invention may conveniently be made by a process wherein one mole of the metal salt of a 1,2,4 or 1,3,4 thiadiazole 3-5 or 2-5 dithiol is coupled to two moles of a primary or a secondary amine by means of sulphur halide in a two-phase medium comprising water and an organic solvent which is substantially immiscible with water. We prefer that the amount of immiscible solvent is at least 10 volume % of the total volume of the two-phase medium. The 1,2,4 thiadiazole -3,5-dithiol itself can conveniently, be prepared by reacting cyanamide with carbon disulphide in the presence of an alkali or alkaline earth metal hydroxide and sulphur. The metal from which the metal thiolate is derived can be any metal but is preferably an alkali metal or an alkaline earth metal, for example sodium, potassium, magnesium, calcium or barium. The thiolate of the 1,3,4 thiadiazole may be prepared by the reaction of hydrazine, carbon disulphide and a metal base or hydroxide such as sodium hydroxide. Thus

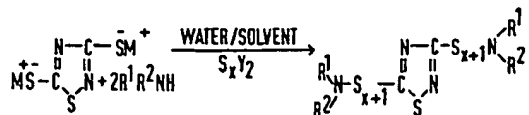


The primary or secondary amines with which the metal thiolate is reacted can be represented by the formula  $R^1R^2\text{NH}$  where  $R^1$  and  $R^2$  which may be the same or different, are hydrogen atoms or hydrogen- and carbon-containing groups provided  $R^1$  and  $R^2$  are not both hydrogen. We prefer that when neither  $R^1$  and  $R^2$  is a hydrogen atom they be hydrocarbyl groups i.e. contain no atoms other than hydrogen and carbon, although  $R^1$  and  $R^2$  may contain other atoms, e.g. oxygen, sulphur phosphorus or nitrogen atoms. The groups  $R^1$  and  $R^2$  can be aliphatic or aromatic e.g. they may be alkyl, aryl, aralkyl or alkaryl groups. If alkyl, the groups  $R^1$  and  $R^2$  preferably contain from 1 to 25 carbon atoms and they may be straight or branched chain. If alkaryl or aralkyl the groups  $R^1$  and  $R^2$  preferably contain from 1 to 18 carbon atoms in the alkyl part of the chain which may be straight or branched. Alternatively,  $R^1$  and  $R^2$  may be part of a nitrogen and carbon-containing ring, e.g. a morpholine, thiomorpholine, piperidine or piperazine ring.

Suitable primary and secondary amines are for example ethylamine, cyclohexyl amine, n-butyl amine, s-butylamine, t-butylamine, t-octyl amine, dodecylamine, diethylamine, di-n-butylamine, di-n-amylamine, di-hexylamine, di-cyclohexylamine, benzylamine, hexamethyleneimine, aniline, toluidine, diphenylamine, alkylated diphenylamine, methyl piperazine and dimethylmorpholine.

In preparing our preferred products by our preferred process one mole of the metal thiolate and two moles of the primary or secondary amine are added to the two phase medium, the thiolate dissolving in the water and the amine dissolving in the organic solvent, and/or the water. The sulphur halide is then slowly added, the reaction temperature can vary, but is preferably between  $10^\circ\text{C}$  and  $50^\circ\text{C}$  e.g. about  $30^\circ\text{C}$ .

The sulphur halides may be represented by the formula  $S_X Y_2$  where X is 1, 2, 3 or 4, and Y is halogen, preferably chlorine e.g.  $SCl_2$ ,  $S_2Cl_2$ ,  $S_3Cl_2$ ,  $S_4Cl_2$  and the following reaction occurs:



where M is a metal and may as shown be monovalent or divalent in which case one metal cation will react with the thiadiazole nucleus.

The compounds may also be made by reacting an anhydrous metal salt of a 1,2,4 thiadiazole -3-5 dithiolate or 1,3,4 thiadiazole 2-5 dithiolate with sulphur dichloride and then reacting the product of this reaction with two moles of a primary or secondary amine both reactions being carried out in a non-aqueous medium.

Products where  $R^3$  is hydrogen or a hydrocarbyl group may be prepared by similar reactions in which one mole of the appropriate thiadiazole derivative is reacted with one mole of the primary or secondary amine.

The choice of the groups R,  $R^1$  and  $R^2$  will depend upon the use to which the product is to be put. The compounds of our invention are useful as chemical intermediates and may also have use as rubber accelerators and lubricant additives. We are particularly concerned with the use of these compounds as lubricant additives where they have been found to be particularly useful as corrosion inhibitors.

The present invention therefore also provides a lubricating composition comprising from 99.99 wt % to 90 wt % of a lubricating oil and from 0.01 to 10 wt % of a compound of the present invention.

The lubricating oil in which the compounds are used is usually a mineral lubricating oil but it may for example be an oil ranging from petroleum oil to SAE 30, 40 or 50 lubricating oil grades or a castor oil, fish oil or an oxidised mineral oil. The compounds are however equally useful with synthetic ester lubricating oil including di-esters such as di-octyl adipate, di-octyl sebacate, didecyl azelate, didecyl adipate, didecyl succinate, didecyl glutarate and mixtures thereof. Alternatively the synthetic ester can be a polyester such as that prepared by reacting polyhydric alcohols such as trimethylol propane and pentaerythritol with monocarboxylic acids such as butyric acid to give the corresponding tri- and tetra-esters. Also complex esters may be used, such as those formed by esterification reactions between a dicarboxylic acid, a glycol and a monohydric alcohol or a monocarboxylic acid.

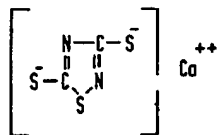
The lubricating oil composition may contain other additives for example dispersants such as the reaction product of polyisobutenyl succinic anhydride with tetraethylene pentamine and the reaction product of polyisobutenyl succinic anhydride with pentaerythritol; antiwear agents such as zinc dialkyl dithio phosphates; antioxidants such as phosphorus pentasulphide treated alpha pinene, p,p' dioctyl diphenylamine and 2,6-di-t-butylphenol; and viscosity modifiers such as ethylene-propylene copolymers.

The compounds may also be used as corrosion inhibitors in fuel oil, such as a petroleum fuel oil, e.g. a diesel fuel. Usually it is present as a minor proportion by weight.

The present invention is illustrated but in no way limited by reference to the following examples.

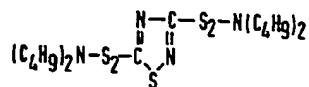
#### Example 1

3,5-bis di-n-butyl-thiosulphenamide of 1,2,4 thiadiazole was prepared by reacting 18.8 grams of:



with 25.8 grams of di-n-butylamine and 11.2 grams of potassium hydroxide in a solvent mixture comprising 300 ml of water and 300 ml of methylene dichloride and

then adding dropwise 20.6 grams of sulphur dichloride in a 50 ml of methylene dichloride. The methylene dichloride layer was separated, dried and the solvent removed by evaporation to yield a compound which analysis was found to contain 47.44% carbon, 7.71% hydrogen, 10.65% nitrogen and 33.1% sulphur; and whose mass spectrum showed a mixture of compounds containing predominantly



#### Example 2

18.8 grams of the calcium salt used in Example 1 were slurried in 400 ml of dry methylene chloride at room temperature and under nitrogen and 20.6 grams of sulphur dichloride in 50 ml of methylene chloride were then added over a period of half an hour. The mixture was allowed to stand and 51.6 grams of di-n-butylamine in 100 ml of methylene chloride added and the mixture stirred for one hour, while held at a temperature between 10 and 20°C. The methylene chloride was then removed with nitrogen and the product separated and analysed and found to contain 45.57% carbon 7.61% hydrogen, 1.17% nitrogen and 33% sulphur with a similar infra red spectrum to the product of Example 1.

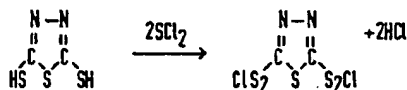
#### Example 3

The anti-wear and corrosion properties of the product of Example 1 in a lubricating oil containing 6% by weight of a conventional polyamine dispersant was tested in the four ball test machine wherein the mean wear scar diameter was measured under a load of 120 kilograms for 1 minute. The copper and lead corrosion properties were measured by determining the weight loss of standard metal sample or copper and lead immersed in the oil for 20 hours at 325°F whilst air was blown through the oil at a rate of 0.25 cu.ft./air hour.

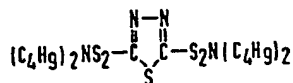
A similar oil but containing none of the compound of Example 1 was subjected to the same tests. The test results are given in Table 1.

#### Example 4

66.5 grams of the 2,5 dithiol of 1,3,4 thiadiazole were slurried with 500 mls of dry toluene and the temperature held below 10°C. 91.3 grams of sulphur dichloride were added slowly to this slurry which was sprayed with nitrogen to remove the hydrochloric acid formed in the reaction.



The mixture was allowed to stand at room temperature for  $\frac{1}{2}$  hour to remove all hydrochloric acid. 114 grams of di-n-butylamine were then added whilst maintaining the nitrogen sparge. Excess amine was added to ensure removal of hydrochloric acid and the reaction mixture filtered to yield 149 grams of a solid soluble in water. On evaporation a dark red liquid containing some solid was obtained and thin layer chromatography, elemental analysis and ultra violet spectroscopy showed this to be a mixture of the amine hydrochloride, the thiadiazole sulphenyl chloride and the 2,5 thiosulphenamide of 1,3,4 thiadiazole of formula



#### Example 5

496 grams of potassium hydroxide were dissolved in 300 mls of water and 86 grams of the disodium salt of the disulphite of 1,3,4 thiadiazole added. 600 mls of methylene dichloride containing 114 grams of dibutyl amine were added and the mixture stirred vigorously. 91.3 grams of sulphur dichloride were then added over a period of 1 hour while the temperature increased from 20°C to 38°C. After completion of addition the mixture was stirred for one further hour.

The methylene dichloride layer was separated off, washed with water, dried

over magnesium sulphate filtered and stripped in a roto-evaporator to yield 213 grams of a dark brown liquid which crystallised on cooling.

Thin layer chromatography, nuclear magnetic resonance spectroscopy and ultra violet analysis showed the product to be a mixture containing both the 2,5 sulphenamide and the 2,5 thiosulphenamide of 1,3,4 thiadiazole.

#### Example 6

350 grams of an aqueous solution containing 24.6 wt % of the disodium salt of the 3,5 dithiol of 1,2,4 thiadiazole was evaporated to dryness, ground and slurried in 50 mls of dry toluene at 10°C. 91.3 grams of sulphur dichloride were added from a dropping funnel whilst the mixture was sparged with nitrogen.

114 grams of dibutyl amine were added from a dropping funnel and the final mixture washed with water, separated direct over magnesium sulphate and evaporated down to yield a product whose analysis showed it to be a mixture containing

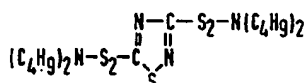
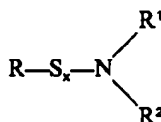


TABLE 1

Additive	wt % of additive	4 Ball Scar diameter mm	Lead Corrosion Pb Loss mg
None		3.0	5000
Example 1	0.5	1.80	1

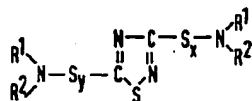
#### WHAT WE CLAIM IS:—

1. Compounds of the general formula



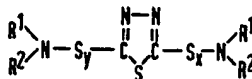
where X is from 2 to 5 and R is a 1,2,4 or 1,3,4 thiadiazole nucleus which may be substituted and R<sup>1</sup> and R<sup>2</sup> are hydrogen or hydrogen and carbon containing groups providing R<sup>1</sup> and R<sup>2</sup> are not both hydrogen or R<sup>1</sup> and R<sup>2</sup> form a heterocyclic ring with the nitrogen to which they are attached.

2. Compounds according to claim 1 of the formula



where y is from 1 to 5.

3. Compounds according to claim 1 of the formula



where y is from 1 to 5.

4. Compounds according to any of the preceding claims in which R<sup>1</sup> and R<sup>2</sup> are both alkyl groups.

5. A process for the production of compounds according to any one of the preceding claims comprising coupling the metal salt of a 1,2,3 or 1,2,4 thiadiazole 3—5 or 2—5 dithiol with a primary or secondary amine by means of a sulphur halide in a two-phase medium comprising water and an organic solvent which is substantially immiscible with water.

6. A process according to claim 5 for the production of compounds according to claims 2 or 3 wherein 2 moles of the primary or secondary amine is coupled with one mole of said metal salt.

7. A process according to claim 5 substantially as hereinbefore described with particular reference to Examples 1, and 5.

5 8. A process for the production of compounds according to any one of claims 1 to 4 comprising reacting an anhydrous metal salt of a 1,2,4 thiadiazole 3—5 dithiolate or 1,3,4 thiadiazole 2—5 dithiolate with sulphur dichloride and reacting the product of this reaction with a primary or secondary amine, both reactions being carried out in a non-aqueous medium. 5

10 9. A process according to claim 8 substantially as hereinbefore described with particular reference to Examples 2, 4 and 6.

10 10. A compound according to claim 1 whenever prepared by a process according to claim 5 to 9. 10

11. A compound according to claim 1 substantially as hereinbefore described with particular reference to Examples 1 and 2.

15 12. A compound according to claim 1 substantially as hereinbefore with particular reference to Examples 4 to 6. 15

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